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Field evaluation of the availability for corn and soybean of phosphorus recovered as struvite from corn fiber processing for bioenergy

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Field evaluation of the availability for corn and soybean of phosphorus recovered as struvite from corn fiber processing for bioenergy

by

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DEDICATION

I would like to dedicate this Thesis to the memory of my father,

Daniel Jefferson Thompson; a great Dad, a progressive farmer and agronomist,

and a wonderful person who inspired so many around him.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1: GENERAL INTRODUCTION

INTRODUCTION

Management decisions concerning phosphorus (P) fertilization have a strong impact on the profitability of crop production and water quality. Continued improvements on yield potential through new cultivars and an increase in grain prices have encouraged growers to adopt more intensive use of inputs including P fertilizers. Also, increased confined animal production, or its concentration in certain areas, has increased the amount of manure P being applied to fields. Consequently, in many areas of the country the P application rates have been increasing. Nonpoint-source P loss from agricultural fields has become a serious threat for water resources and great public concern. Thus, P-related future sustainability of agriculture and the environment is based on two major challenges: more efficient use of agricultural P sources and extensive recovery of P from livestock and bioenergy byproducts or waste. Phosphorus can be recovered as struvite ($NH_4MgPO_4.6H_2O$) from the aqueous stream of these operations. A low P water-solubility in struvite, and early greenhouse research with some forms of struvite, suggested a slow-release of P for plants. However, recent short-term greenhouse studies found similar P plant-availability for triple superphosphate (0-46-0) and struvite (Johnston and Richards, 2003; Barak and Stafford, 2006; Tabatabai et al., 2009).

In spite of several greenhouse studies, no published research was found assessing at the field level the value of struvite as a P fertilizer by comparing it with conventional P fertilizers in corn-soybean rotations. Therefore, the objective of this study was to evaluate at the field the P availability for corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] of P recovered as struvite from the aqueous stream of corn fiber processing for bioenergy by comparing it with P fertilizer.

THESIS ORGANIZATION

This thesis is presented as a paper suitable for publication in scientific journals of the American Society of Agronomy or Soil Science Society of America. The title of the paper is Field Evaluation of the Availability for Corn and Soybean of Phosphorus Recovered as Struvite from Corn Fiber Processing for Bioenergy. The paper includes sections for an abstract, introduction, materials and methods, results and discussion, conclusions, references, tables, and figures. It is preceded by a general introduction and is followed by a general conclusion.

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CHAPTER 2: FIELD EVALUATION OF THE AVAILABILITY FOR CORN AND SOYBEAN OF PHOSPHORUS RECOVERED AS STRUVITE FROM CORN FIBER PROCESSING FOR BIOENERGY

A paper to be submitted to Soil Science Society of America Journal

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ABSTRACT

There is strong interest on recovering nutrients from waste stream of industrial processing of crop biomass for bioenergy so it can be efficiently utilized as a fertilizer material. The objective of this study was to evaluate at the field the P availability for corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.] of P recovered as struvite ($NH_4MgPO_4.6H_2O$) from the aqueous stream of corn fiber processing for bioenergy. Trials were established at three Iowa locations with different soil series. Soil-test P (STP) was low (8 to 12 mg kg^{-1} Bray-1 P, 15-cm depth) and pH was 5.5 to 6.4. Each trial was evaluated for three years, with corn the first year, soybean the second, and corn the third. Treatments were 0, 12, 24, 36, 48, 72, and 120 kg P ha^{-1} as granulated struvite or triple superphosphate (TSP) P sources, which were broadcast and incorporated into the soil only once before the first corn crop. Measurements were corn aboveground dry matter accumulation (DW), P concentration, and P uptake at the V6 growth stage only the first year; grain yield, P concentration, and P accumulation; and post-harvest STP each year by the Bray-1, Mehlich-3 (M3), and Olsen tests. There were very large P rate

effects on all plant and soil measurements at the three sites ($P \leq 0.01$). The two P sources did not differ for any plant measurement or, occasionally, values for struvite were higher than for TSP with similar P rates applied. We conclude that P recovered as struvite from corn processing for bioenergy has crop P availability similar to inorganic P fertilizer or higher.

Abbreviations: DAP, diammonium phosphate; DW, dry matter; LP, linear-plateau; MAP, monoammonium phosphate; M3, Mehlich-3 P; OM, organic matter; QP, quadratic-plateau; STP, soil-test P; TSP, triple superphosphate.

INTRODUCTION

Phosphorus is an essential plant nutrient and is needed for nucleic acids and the metabolism of energy production and transfer in plants. Although P is considered a macronutrient, P concentrations in plant tissues and uptake are substantially lower than for the macronutrients N and K. Moreover, in most agricultural areas, soils have low levels of crop available P, hence application fertilizer or manure P is critical to improve crop production (Chien et al., 1990; Johnston and Richards, 2003). Based on national yield averages (National Agricultural Statistics Service, 2013) estimated P removal (Sawyer et al., 2002) with grain production in United States for corn (assuming an average yield of 9.41 Mg ha^{-1}) is 26 kg P ha^{-1}, for soybean (assuming yield of 2.69 Mg ha^{-1}) is 15 kg P ha^{-1}, and for wheat (assuming yield of 3.02 Mg ha^{-1}) is 12 kg P ha^{-1}, which might be higher in regions where the climate allows two crops a year. As a result, agriculture is highly dependent on P fertilizer, primarily derived from phosphate rock, a non-renewable resource. The exact timing of peak P production and remaining reserves is disputed, but it is widely acknowledged by the fertilizer industry that the quality of remaining phosphate rock is decreasing and production costs are increasing (Cordell et al., 2009). At the same time, inappropriate management of P fertilizer and manure has become a serious threat to water quality in many areas. Nonpoint-source P loss from agricultural fields has the potential to accelerate eutrophication of freshwater ecosystems. In the United States, a 1998 water quality USEPA report cited agriculture as the primary source of pollution in 60% of impaired river miles, 30% of the impaired lake acres, and 15% of estuarine square miles (Parry, 1998). Phosphorus has received a great deal of attention due to its role as the limiting nutrient in many freshwater ecosystems (Nassauer et al., 2002; Cruse and Herndl, 2009). As of 2006, the Iowa Department of Natural Resources considered 282 Iowa surface water bodies impaired for a number of reasons, including excessive P concentration Runoff phosphorus loss immediately after poultry manure application as influenced by the application rate and tillage (Kaiser et al., 2009).

Future P scarcity and potential water pollution have increased interest in the recovery of P from sewage of urban areas, effluents of livestock facilities, and various industrial processes. There have been many advances in the technology available to recover P before these materials are applied as waste to fields, thus reducing the threat to water quality (Burns and Moody, 2002; Zhang et al., 2010). A potential area of focus for P recovery is the discharge and waste originating from bioenergy production plants. According the U.S.D.A the production of biofuels in USA has grown from 1.749 billion gallons per year in 2000 to 14 billion gallons per year in 2012, a net total growth of

800% in only 12 years, and ethanol produced from corn grain represents 98% of the total production (Economic Research Service, 2013).

Different chemical approaches can be taken to recover P by precipitating soluble P in various chemical forms. These include magnesium ammonium phosphate and magnesium potassium phosphate, members of a group of related compounds called struvites, although the composition of pure struvite is $MgNH_4PO_4.6H_2O$ (Johnston and Richards, 2003). More than 150 years ago, struvite was first discovered in sewer systems in Hamburg, Germany, and was named for geographer and geologist Heinrich Christian Gottfried von Struve (1772-1851) (Barak and Stafford, 2006). Rawn et al. (1939), cited by Barak and Stafford (2006), describes struvite generated in sewage treatment plants and pipes from the anaerobic digestion of solids which results in the release of ammonium and phosphates and precipitation as struvite. Struvite is found in human urinary sediments and some kidney stones, which sometimes are associated with infections of the urinary tract and high levels of urine pH. It can also be found in canned seafood, where phosphates react with Mg and Na since sea water is rich in these elements (Lampila, 1993). “Guanite” is a form of struvite found in manure of seabirds (commonly known as “guano”) storage facilities. Although it is still unclear if this struvite is formed directly from the animal’s excretions or is product of the microbial decomposition of manure (Bridger et al., 1962; Barak and Stafford, 2006).

Struvite can precipitate naturally in soils in the presence of high concentrations of soluble P, ammonium, and Mg. Struvite in soil may be inherited from soil parent material or can be formed when ammonium phosphates are applied under neutral to alkaline conditions. Highly water soluble monoammonium phosphate (MAP) and diammonium phosphate (DAP) react with soil solution Mg forming struvite (Lindsay and Taylor, 1960). Phosphorus also can be precipitated as Al, Ca, and/or Fe phosphates. However, unlike struvite, the P in these materials may not be highly soluble in water or available for crops. In most situations however, techniques to improve struvite recovery from discharges of municipal sludge, even from livestock and industrial operations, must include the addition of Mg and methods to increase the pH. Removing CO_2 from liquid discharges by aeration is a low-cost way to raise pH above 7.5 (Barak and Stafford, 2006).

Considering the chemical composition of struvite, its removal by precipitation will simultaneously reduce both the N and P content of the leftover sludge. Due to the initial proportions of both nutrients, this process will generally have a marginal effect on N, and a much greater impact on the P concentration of the resulting sludge (Barak and Stafford, 2006). Compared with recovery of other nutrients, a significant benefit of recovering struvite-P is the relative simplicity of its production, its purity, and its relatively high P concentration (De-Bashan and Bashan, 2004; Winker et al., 2009). Peng et al. (1979) mentioned by Barak and Stafford (2006) have shown that recovered struvite has low concentration of P soluble in water, and identified struvite as a slow-release P fertilizer. The same authors also mentioned that in the 1960s, WR Grace & Co. marketed an ammonium/potassium magnesium phosphate fertilizer as a slow-release fertilizer under the trade name of MagAmp. Often struvite is considered a “slow-release fertilizer, though there is limited evidence for this categorization. According to Gell et al., (2011), struvite from a varied list of sources had proven to be a good source of P in several studies (Bridger et al., 1962; Terman and Taylor, 1965; Ghosh et al., 1996; Goto, 1998; Johnson and Richards, 2003; Li and Zhao, 2003; Romer, 2006; Gonzalez-Ponce and Lopez-de-Sa, 2007; Montag et al., 2007; Plaza et al., 2007; Ganrot et al., 2007; Ponce and Lopez-da-Sa, 2007; Cabeza Perez et al., 2009; Massey et al., 2009; Gonzalez-Ponce et al., 2009; Weinfurtner et al., 2009; Yetilmezsoy and Sapci-Zengin, 2009 and 2010).

Usually P fertilizers are classified in two categories according their water solubility: soluble forms (such as triple superphosphate and ammonium phosphates) and slightly soluble forms such as rock phosphate. The same authors concluded that struvite did "not readily fit into either category since it has low solubility (Rondeltap et al., 2007) but can decompose quickly to soluble fertilizers (Cabeza Perez et al., 2009; Johnston and Richards, 2003)". In a greenhouse pot experiment using a P-deficient Plano silt loam soil, which is commonly found in Illinois and south-central Wisconsin, Barak and Stafford (2006) compared struvite and DAP fertilizer by measuring corn dry matter yield, P concentration in plant dry matter, P uptake in above ground dry matter, and residual soil Bray P in the soil. The struvite used in this study was obtained by crystallization from a supersaturated solution of magnesium sulfate and ammonium phosphate, and processed to match the particle size of the DAP. In addition to controls with no P, treatments included two DAP rates and one struvite rate. This study showed that P uptake with 36 mg struvite-P kg^{-1} of soil was equivalent to 42 mg DAP-P kg^{-1} of soil and that, therefore, struvite had a relative efficiency of 117% compared with DAP.

Furthermore, they reported that residual Bray P in soil with 36.4 mg struvite-P kg^{-1} soil was equivalent to 64.9 mg DAP-P kg^{-1}, or a 178% equivalency.

Iowa recent research in Iowa (Tabatabai et al., 2009) chemically characterized struvite recovered from the aqueous stream of corn fiber processing for bioenergy, and compared it with monocalcium phosphate in the greenhouse by measuring corn and ryegrass DW and P uptake for three soils (Clyde, Galva, and Nicollet) and various application rates. The mean water-soluble P of struvite was 6.0 g kg^{-1}, which was 5% of the total P concentration. When struvite P was extracted with 2% citric acid by shaking for 2 h, the extracted P was 99 g kg^{-1}, which was 84% of the total P. This result suggested that most of the P in the struvite samples analyzed would be available to plants. The DW yield and P uptake by both crops increased greatly with increasing P application rates, but there were no differences ($P \leq 0.05$) between the two P sources for any application rate.

In spite of several studies about recovery of P as struvite and greenhouse experiments to determining its value as P fertilizer, no published research was found comparing struvite and fertilizer P for corn and soybean at field conditions and using struvite recovered from crop fiber processing for bioenergy. Therefore, the objective of this study was to evaluate at the field level the P availability for corn and soybean of P recovered as struvite from the aqueous stream of corn fiber processing for bioenergy by comparing it with P fertilizer.

MATERIALS AND METHODS

Sites and Treatments

Three, 3-year field plot trials with corn-soybean rotations were established to evaluate the availability of P in struvite compared with triple superphosphate (TSP) commercial fertilizer. The trials were established at three Iowa State University research farms: the Northeast Research Farm (Floyd County), the Northwest Research Farm (O'Brien County), and the Agricultural Engineering/Agronomy Research farms (Boone County) in Central Iowa. The sites chosen had three different typical Iowa soils which tested Very Low or Low in P according to Iowa State University interpretations (Sawyer et al., 2002). Table 1 shows the most relevant site information. Each trial was evaluated for three years, with corn the first year, soybean the second year, and corn the third year. At Floyd and O'Brien sites, the study began in the spring of 2009 whereas at Boone began in the spring of 2010. The previous crop had been soybean at the three sites. The tillage management was chisel-plowing in the fall and field cultivating before planting in spring for corn residue and only field cultivating in spring for soybean residue. The chisel-plow shanks were spaced 30 cm apart and tilled soil to a depth of 15 to 20 cm. The field cultivators had staggered toolbars with shanks and with overlapping 20-cm wide sweeps and one or two toolbars with thin teeth that smoothed the soil surface. Both crops were planted using 76-cm row spacing, adapted corn hybrids or soybean varieties for each region, plant populations recommended by Iowa State University, and weed control with pre-emergence and/or post-emergence herbicides. Table 2 shows planting dates, cultivars and rainfall data across the sites-years.

Treatments were 0, 12, 24, 36, 48, 72, and 120 kg P ha^{-1} applied as granulated struvite or granulated TSP, which were broadcast by hand 30 days before planting the first corn crop and were incorporated into the soil by the spring field cultivation operation. No P treatment was applied in the following years with only one exception. After soybean was harvested in fall of the second year, 72 kg P ha^{-1} with each source was applied to treatment plots that had received the initial application of 12 kg P ha^{-1}. This was done to assure that maximum yield was archived at least by one treatment in all years of the study. Each plot was 4.56 m (6 rows) wide at Floyd County and 6.08 m (8 rows) wide at the O'Brien and Boone sites, and all were 15 m in length. The P source and P rates treatment combinations were arranged in a randomized complete-block design with three replications at Floyd County and O'Brien sites and four replications at the Boone site. The struvite source used was the same that was used in the Iowa greenhouse study referred to before (Tabatabai et al., 2009) except that this was granulated. It had 47 g kg^{-1} moisture, 117 g kg^{-1} total P, 6.0 g kg^{-1} water-soluble P, 99 g kg^{-1} P soluble in 2% citric acid, and pH 6.9. More complete struvite analysis by Tabatabai et al. (2009) showed it had 0.51 g kg^{-1} total C, 71 g kg^{-1} total N, 38 g kg^{-1} total K, 153 g kg^{-1} total Mg, and 2.5 g kg^{-1} total S. The struvite granule size ranged from 1 to 5 mm with an average of 2.25 mm, and the material had 1.15 g ml^{-1} density. The TSP granule size had a similar range but a slightly larger average size (2.75 mm), and the material had higher density (1.76 g ml^{-1}).

The soils at the sites tested Optimum or High in K according to Iowa interpretations for corn and soybean, and no soil test for Mg or S is recommended in

Iowa (Sawyer et al., 2002). However, the first year we applied 80 to 100 kg K ha^{-1} (KCl), 34 kg Mg ha^{-1}, and 44 kg S ha^{-1} (both Mg and S as hydrated magnesium sulfate, $MgSO_4•7H_2O$). A N rate of at least 168 kg N ha^{-1} was applied to all corn crops (as anhydrous ammonia).

Soil, Plant, and Grain Yield Measurements

Before any treatment was applied, composite soil samples (12 cores, 0-15 cm depth) were collected from each replication (three per sites) and were analyzed separately, but the average was used to represent initial soil-test values for each site (Table 1). Soil samples were dried at 40 °C and crashed to pass through a 2- mm sieve. These samples were analyzed for various properties following procedures recommended for the North Central Region by the NCERA-13 regional soil testing and plant analysis regional committee. Soil-test P was measured by the Bray-P1, Mehlich-3, and Olsen methods using a colorimetric determination of extracted P (Frank et al., 1998); K, Ca, Mg, and Na were measured by the Mehlich 3 method (Warncke and Brown, 1998); and pH by the 1:1 soil-water ratio method (Peters et al., 2012). Soil organic matter (OM) was measured by a combustion method described by Wang and Anderson (1998). Soil particle size was measured on a single composite sample for each site by the hydrometer method (Bouyoucos, 1962).

The first year, a composite sample of the above-ground corn plant portion was sampled at the corn V5 to V6 grow stage (Abendroth et al., 2011). Ten plants were collected from rows from which corn would not be harvested but border rows were avoided. Plant samples were dried in a forced-air oven at 60 °C, weighed, and ground to pass through a 2 mm screen. The total concentration of P and other nutrients in the plant tissue were measured by digesting samples with concentrated HNO_3 (Zarcinas et al., 1987) and analyzing for nutrients in the digests by inductively coupled plasma spectrometry. Phosphorus uptake at this growth stage was measured from the plant dry weights and P concentrations. Corn and soybean grain was harvested from a central area of each plot with a plot combine. A subsample of grain was collected for determination of moisture and P concentration. Grain yields were adjusted to 155 or 130 g kg^{-1} moisture for corn or soybean, respectively.

Data Management and Statistical Analysis

Analyses of variance of treatment effects on the measurements for a randomized complete-block design assuming fixed treatments effects and random block effects were performed for each site and year using the MIXED procedure of SAS (SAS Institute, 2008). Sources of variation in the model were blocks, P source, P rate, and the interaction between source and rate. When the P rate main effect was significant at $P \leq 0.05$, the measurements response to applied P was described by fitting linear, quadratic, linear-plateau (LP), and quadratic-plateau (QP) models. The models were fit to P rate means across both P sources when the P source main effect or the interaction between source and rate was not significant at $P \leq 0.05$, and to P rate means for each source when either the source or the interaction was significant. The models were fit using the REG (for linear and quadratic) or NLIN (for LP and QP) procedures of SAS (Cerrato and Blackmer, 1990; SAS Institute, 2008). We chose quadratic, LP or QP models to describe a crop response only when the residual sums of squares were significantly smaller (at *P*

≤ 0.05) than for the linear model. When the three complex models were significantly better than the linear model, we chose the one with highest adjusted R^2 (SAS Institute, 2008), but did not choose the quadratic model when it predicted a decrease after a maximum within the range of P rates used this was not clear from the observed data because this is a well- known problem for this model (Cerrato and Blackmer, 1990). The same procedures were used to describe the mean response of some measurements to P across years of a site or across sites.

RESULTS AND DISCUSSION

Treatments Effects on Early Growth and P Uptake

Study of early corn plant DW, P concentration, and P uptake data from the first year of the trials showed that P applied as struvite or fertilizer increased all measurements significantly (Table 3). This result was expected because the three soils tested Very Low or Low according to current Iowa interpretations for STP. Analysis of variance for each measurement and site showed that on average across P rates, the two P sources differed only for DW at the Floyd site, where DW was greater for struvite (6.12 g plant^{-1}) than for fertilizer (5.42 g plant^{-1}). The interaction between P source and P rate (either the full interaction or the linear or quadratic components) was significant ($P \leq 0.05$) only for plant DW and P uptake at the Boone site. Data in Table 3 shows that values of both measurements for the highest P rate were greater for struvite than for fertilizer. Orthogonal comparisons for source effects confirmed a difference between P sources for this highest rate but not for any other rate (not shown). At the Floyd site, a significant P source effect but no interaction for DW and P uptake would indicate that something in the struvite determined a greater DW and P uptake for struvite. However, this difference was due to a very large difference mainly for DW between struvite and fertilizer for the highest P rate (Table 3). Orthogonal comparisons for source effects on DW and P uptake for the highest P rate were significant for both measurements ($P \leq 0.01$) but were not significant for any other rate (not shown). Therefore, we conclude that at the Floyd site the DW and P uptake responses to P were greater for struvite but only for the highest P rate. A similar difference also was apparent at O'Brien, but it did not reach significance at $P < 0.05$.

Based on the results, we fit P response models for each site and measurement separately for each source when the interaction or the source comparison for the highest P rate was significant, but fit models for struvite and fertilizer pooled together when the interaction was not significant. Table 3 shows the relevant statistics for these models and the P rate that resulted in the maximum estimated value. All models fit to responses to struvite were linear or quadratic with no predicted maximum within the range of P rates applied. Most models fit to responses to fertilizer did not have a maximum within the range of P rates applied except for two instances. The exceptions were quadratic models with a predicted a decrease consistent with observed data for fertilizer P for DW and P uptake at Boone.

Given the clearly different type of response observed for DW and P uptake between the Boone site and the other two sites, and to visualize better the responses, Fig. 1 shows data for Boone and averages for Floyd and O'Brien sites (from Table 3). Several important results become clear from this figure. One is that the plant P concentration response was always similar for struvite and fertilizer and increases curvilinear up to the maximum P rate applied. Another result is that the highest P rate applied with struvite increased DW and P uptake more than with fertilizer. Plant P uptake followed very closely the DW responses and not the P concentration responses, because P effects were proportionally greater for DW than for P concentrations.

The results showed a similar or higher efficiency of struvite at increasing early plant DW and P uptake compared with fertilizer. Based on the data in Table 3, struvite plant P uptake was 4% higher than fertilizer P uptake on average across all P rates and sites. However, a similar calculation for the highest P rate indicated that P uptake was 21% higher for struvite than for fertilizer.

Based on greenhouse studies, struvite precipitated from municipal waste sludge was categorized as a “viable slow-release fertilizer” (Ronteltap et al., 2010; Gell et al., 2011), and it was suggested that it can be effectively used at high applications rates without risk of damaging plants (Özden et al., 2007; Ronteltap et al., 2010; Gell et al., 2011). The previous Iowa greenhouse study with the same struvite and fertilizer sources (but not granulated) showed similar efficiencies at increasing DW and P uptake with corn and ryegrass (Tabatabai et al., 2009). We cannot explain with certainty the apparent greater efficiency of the highest P rate applied with struvite compared with fertilizer, at increasing early plant DW at all our field sites for the highest P rate applied. This difference was most evident at Boone, where the highest fertilizer rate actually decreased plant DW (and P uptake) compared with a similar struvite P rate and also compared with the second-highest fertilizer rate. Research has shown that high rates of soluble P may induce Zn deficiencies with negative effects on plant growth (Warnock, 1970; Loneragan et al., 1979; Loneragan and Webb, 1993). Warnock (1970) reported that Zn deficiencies can be associated with high Fe concentrations in plant tissue, and that this P-Zn interaction altered the mobility and accumulation of the micronutrients Mn, Fe, and Zn within the plant. However, in our study, we couldn’t find any obvious relationship between micronutrient concentrations in the plant tissue and DW differences due to struvite or fertilizer application (not shown).

Treatment Effects on Grain Yield, P Concentration, and P Accumulation

First Year Results

Results for the first year of the trials showed very large responses of corn grain yield, P concentration, and P accumulation to P applied as struvite or fertilizer (Table 4). Large increases were expected because STP values were below Optimum for corn and soybean according to ISU soil-test interpretations (< 16-20 mg kg^{-1} by the Bray and M3 tests, and < 11-14 mg kg^{-1} by the Olsen test), and responses agree with previous research with P fertilizer (Mallarino and Blackmer, 1992; Dodd and Mallarino, 2005; Kaiser et al., 2005). Yield levels varied across sites. The mean trial yield was higher at Floyd (13.44 Mg ha^{-1}), intermediate at O’Brien (11.62 Mg ha^{-1}), and lowest at Boone (9.55 Mg ha^{-1}). At Floyd, rainfall was below normal during the 2009 growing season but was above normal for the months of June and July (Table 2), during which water availability is a major determinant of corn yield. Corn yield often is lower in northwest Iowa (O'Brien site) due to lower average rainfall compared to the other regions (Table 2).

Yield at the Boone site often is low in years with excess rainfall since the Webster soil is poorly drained. In 2009 at O'Brien and in 2010 at Boone sites excess rainfall in early spring (Table 2) or small amounts in consecutive days delayed planting by two weeks over the planned planting date, whereas corn at the Floyd site was planted at the planned time. Then, higher than normal rainfall during May at O'Brien and June at Boone may have limited corn growth and development compared with the Floyd site. At Boone, for example, rainfall in June, July, and August 2010 was one of the highest on record with 741 mm (the average rainfall over the last 30 years for this period was 377 mm).

Analysis of variance for each measurement and site showed that on average across all P rates the two P sources differed ($P \leq 0.05$) only at the Boone site (Table 4), where grain yield and P accumulation were greater for struvite than for fertilizer although the difference was small for yield (0.67 Mg ha^{-1}) and very small for P accumulation (1.54 kg ha^{-1}). The interaction between P source and P rate also was significant ($P \leq 0.05$) only at the Boone site and for both grain yield and P accumulation, which was explained by the larger response with struvite then with TSP for the highest P application rate. Data, types of response model, and estimated P rates to achieve a maximum in Table 4 shows that at Floyd and O'Brien sites (where there were no source differences) yield increased following a QP type of response up to a maximum at 46.9 and 97.1 kg P ha^{-1}, respectively, whereas grain P concentration and P accumulation increased linearly or in a curvilinear manner up to the highest P rate applied (120 kg P ha^{-1}). At Boone, however, the yield response to struvite P followed a QP type of response (plateau reached with 60.9 kg P ha^{-1}) whereas yield for TSP reached a maximum with 57.8 kg P ha^{-1} and then decreased sharply. The grain P concentration increased exponentially for both sources. Although the grain P accumulation with struvite also increased exponentially, with TSP (as for yield) the P accumulation reached a maximum with 64.4 kg P ha^{-1} and then decreased sharply. The different yield and P accumulation responses to struvite and TSP at Boone match observed early plant DW responses (Table 3 and Fig. 1). As we discussed for DW responses, soil properties and the concentrations of other nutrients in grain did not help explain the yield decrease by the highest TSP rate. This yield decrease at the highest TSP rate was due to the small size of the ears and the reduced number of kernels per ear. There was no lodging and the number of plants for plots receiving the highest TSP rate did not show significant differences relative to the other treatments (not shown).

Given the different type of response observed at Boone compared with Floyd and O'Brien sites, and to visualize better the responses, Fig. 1 shows data for Boone and averages for Floyd and O'Brien sites (from Table 4). Several important results become more evident from this figure than from Table 4. One is the contrastingly different grain yield response to TSP observed at Boone compared with yield response to struvite at this site and to the average response to TSP or struvite at the other sites (for which the source of interaction effects were not significant at $P \leq 0.05$). Another important result was the large P effect at increasing grain P concentration, which increased up to the highest P rate applied, although a curvilinear increase was more pronounced at Boone than for the average of data from Floyd and O'Brien sites. Finally, the response to P of grain P accumulation reflected better the yield responses than P concentrations because the relative magnitudes of the differences were greater for yield.

Second and Third Year Results

The second and third years of the trials continued evaluating struvite and TSP as sources of P for corn and soybean by comparing residual effects of P applied before the first-year corn crop on grain yield, grain P concentrations, and P accumulation in grain. Table 5 shows data for the second-year soybean crop. Soybean at the O'Brien site suffered the consequences of excess rainfall (235 mm in June and 127 mm in July, Table 2) in a moderately poorly drained soil, which resulted in low and uneven yield (3.12 Mg ha^{-1}). However, average soybean yield at Floyd was very high (4.69 Mg ha^{-1}) and was high at Boone (4.24 Mg ha^{-1}).

The three grain measurements showed large and significant increases from P applied before the first year corn (there was no new P application for soybean). In contrast to first-year results, when at the Boone site the highest TSP rate reduced corn yield compared with lower rates or the highest struvite rate, the P sources did not differ and the P source by P rate interaction was not significant ($P \leq 0.05$) for any measurement at any site. The highest P rate applied the previous year (120 kg P ha^{-1}) maximized values of most measurements and the responses were linear or curvilinear with decreasing increments to a maximum at higher rates. The only exception was for grain yield at Floyd, where the increase was curvilinear up to a rate of 63.5 kg P ha^{-1} at which a plateau was reached.

Table 6 shows data for the third-year corn crop. As for the first year, the mean corn yield was higher at Floyd (13.38 Mg ha^{-1}), intermediate at O'Brien (11.87 Mg ha^{-1}), and lowest at Boone (10.73 Mg ha^{-1}). Both in 2011 (Floyd and O'Brien sites) and 2012 (Boone) April received frequent rainfall (although not necessarily excessive) that delayed planting to May (Table 2). This delay did not affect yield much at Floyd but resulted in only moderate yields at O'Brien and Boone sites. For the Boone site it is noteworthy that high but not excessive rainfall in April 2012 and a later than normal planting date seems to have alleviated effects of lower than normal rainfall the rest of the season. Severe drought affected most other areas of the state but the effects were moderate at this site.

To avoid confusion and refer to residual effects on the measurements for all rates, Table 6 does not include data for the initial 12-kg P rate, because we applied additional P to plots of this treatment for this third year to see how residual effects of the initial rates compared with a fresh high P application. Comparisons for all measurements showed no statistical differences ($P \leq 0.05$) between the highest initial 72- and 120-kg P rates and the fresh P rate with only two exceptions. The exceptions were grain yield and P removal at the Boone site, where values for the fresh applied P were lower for both P sources. These results indicate a long positive residual effect for the two highest initial P rates, which is reasonable given STP results that will be discussed in the next section. Similarly to results for the second year, the crop responses in this third year also showed no P source differences and no significant ($P \leq 0.05$) P source by rate interaction for any measurement at any site (Table 6). The highest P rate applied two years earlier (120 kg P ha^{-1}) maximized values of most measurements with linear or curvilinear types of response. The only exception was for grain yield at Boone, where the response was curvilinear up to a rate of 88.3 kg P ha^{-1} at which a plateau was reached.

Since there were no significant source or interaction effects for any grain measurement in the second and third years, Fig. 3 shows means across the three sites for each trial year (from Tables 5 and 6). The highest P rate applied before the first year maximized values of all measurements for both the second and third years, although differences from the second-highest rate were small or large depending on the site and measurement. A response up to a higher initial P rate compared with the first-year responses could be expected mainly in the second and third years because of crop P removal and likely STP decline with no additional P application. The responses to P were linear or curvilinear with smaller increments as the rate increased with only one significant exception. The exception was for grain P concentration in the third year, where the response was curvilinear with increasing increments. This average response across the three sites was explained by a similar type of response, but more pronounced at the Floyd site. Table 5 shows that at Floyd, the soybean grain P concentration was not increased or was increased very little by the lower three rates. We are not sure about reasons for this response, because the slopes of the grain yield responses this third year were approximately similar for the three sites (not shown).

The results showed a similar or higher efficiency of struvite at increasing grain yield compared with fertilizer. Based on the data in Tables 4, 5, and 6, grain yield with struvite was only 0.5% higher than with fertilizer on average across all P rates, sites, and years. A similar calculation for the highest P rate indicated that grain yield was 3% higher with struvite than with fertilizer, however, although this difference was mainly due to the first year (8% higher on average across sites) and to results at Boone (37% higher).

Treatments Effects on Soil-Test P

Soil-Test P-After the First Crop

Phosphorus applications with both sources before the first corn crop had a large effect on postharvest STP. Table 7 contains the STP values and summary ANOVA results. The results from the three soil-test methods at the Boone and Floyd sites showed no differences between the P sources, no interaction P source by P rate, and a linear increase up to the highest P rate applied ($P < 0.05$). Values for M3 and Bray tests were very similar, and ranged from 8.0 mg P kg^{-1} for untreated plots to 17.2 to 18.7 mg P kg^{-1} for the highest P application rate. As expected for these Iowa soils, the Olsen test results were approximately 50% lower than for M3 and Bray values. However, at O’Brien, there were small STP differences between P sources as measured by the Bray and Olsen tests and large source by rate interaction effects for all three tests ($P < 0.05$). The mean STP values for the struvite treatments were slightly lower than the mean values for the TSP treatments (by 2.4 and 2.3 mg P kg^{-1} for BP and Olsen, respectively).

Data in Table 7 and results for the interaction for the three test methods show that these differences mainly were due to differences for the highest P rate, for which STP for struvite was much lower than for TSP. This difference determined a linear increasing trend for struvite but a quadratic trend with increasing increments to a maximum for

TSP. This difference does not match with a lack of source differences for this rate observed for first-year early plant growth and P uptake or with grain yield, P concentration, and P accumulation in the first or third years of the trials; and we could not find a reasonable explanation. The P accumulation with corn grain harvest (Table 4) was almost identical for both sources and (22.1 and 22.2 kg P ha^{-1}). Concerning soil properties (Table 1), the Marcus soil at the O'Brien site had twice the clay concentration, higher (and neutral) pH, and higher OM than the other two soils. Extractable Ca was twice that in the Floyd soil but approximately similar to that in the Webster soil. It is possible that higher pH and Ca content in the Marcus soil at this site could interfere with the P extraction by BP compared with the other two soils. However, the M3P and Olsen tests showed the same relative differences in STP at the O'Brien site as at the other sites, and this effect would occur similarly for both P sources or even more for TSP since its main P compound is mono-calcium phosphate (the struvite main P compound is magnesium phosphate).

Soil-Test P-After the Second and Third Crops

After the second crop was harvested (soybean), the STP values for all sites, rates, and tests clearly declined (Table 8) compared with results for the first year. The STP response model fit for the three P tests changed from often a linear relationship to a slightly curvilinear response with increasing increments as the P rate applied before the first year increased, possibly due to greater effect of grain accumulation of P and removal with harvest at lower P rates. Soil-test P levels by M3 and Bray tests, across all three sites ranged from 7.3 to 9.3 mg P kg^{-1} for untreated plots, 7.5 to 10.7 mg P kg^{-1} for the lowest rate of P (12 P kg ha^{-1}), and 20.9 to 29.8 mg P kg^{-1} for the highest P rate. The Olsen test values again were on average about one-half of the M3 and Bray values. All STP responses were consistently similar at the three sites, with no significant P source differences and no source by P rate interaction ($P < 0.05$). Therefore, an important result for the O'Brien site was that in this second year there was no data or statistical difference between sources for the highest P rate.

Soil-test P results after harvest of the third crop (corn) showed, as expected, a decline in STP levels as measured by all P tests when compared to prior years' results (Table 9). Soil-test P for M3 and Bray ranged from 5.7 to 7.7 mg P kg^{-1} at the untreated plots and from 15.8 to 28.2 mg P kg^{-1} at the highest P rate. On average across all P rates there was no difference between P sources for any soil P test, but an important result was that similarly to results from the first year there was no a significant interaction between source and P rate at Boone and Floyd sites but there was at O'Brien. As in the first year, but in contrast to results from the second year, STP for the highest P rate was lower for struvite than for TSP. As we discussed for first-year results we have no reasonable explanation for this difference, and we feel especially puzzled by the fact that a difference was observed in both corn years but not in the soybean year.

Given the different type of STP response observed at the O'Brien site compared with the other two sites, and to visualize better the responses, Fig. 4 shows data for the three years at O'Brien and Fig. 5 means for each year across Boone and Floyd sites. The contrasting results discussed before become more evident from these two figures. Figure 4 plots the same data shown in Tables 7, 8, and 9 and shows very well the distinct interaction between P source and P rate, which is explained by a difference for the highest P rate, for the three soil-test methods for the two corn years (first and third years) but not for soybean (second year). Figure 5 shows means for each year across the Boone and Floyd sites and demonstrates no evidence for an interaction for any year or soil P test (means from data in Tables 7, 8, and 9). These figures show how the effects of the initial P application on STP diminished over time more consistently for the Boone and Floyd site than for the O'Brien site.

In summary, STP values as a measure of residual P from the initial applications showed no significant differences across the three sites in any of the three years for the 72-kg rate or lower. Results for the highest P rate applied (120 kg P ha^{-1}) showed higher STP levels for TSP fertilizer in two years at one site. However, although such a difference did not match with grain yield, P concentration and P accumulation and could not be reasonably explained.

SUMMARY AND CONCLUSIONS

Results of all corn young plant and grain measurements the first year of the study and of all grain measurements in the second and third years showed that the crop availability of struvite P often was similar to TSP and in a few instances it was higher. Struvite was more efficient than TSP only the first year and for the highest P application rate (120 kg P ha^{-1}) at increasing early DW and P uptake at the three sites and for grain yield and P accumulation only at the Boone site. These differences occurred because these measurements' values for the highest P rate with TSP were lower than with struvite, and this TSP rate often decreased values compared with the next lower TSP rate (72 kg P ha^{-1}). We could not find a reasonable explanation with the soil and plant measurements included in the study. The second and third years of the study (corn and soybean, respectively) did not include early plant measurements and evaluated residual effects of the first-year P applications on grain yield, P concentration, and P accumulation. There were no significant ($P > 0.05$) source or interaction source by P rate effects for any grain measurements in the second and third years, and the highest P rate applied prior to the first year maximized values of all measurements in both years in spite of slight differences in response shapes (linear or curvilinear).

Estimates of the crop P availability of P in struvite and TSP by analysis of soil samples collected postharvest each year by the Bray, M3, and Olsen test methods showed mostly no differences between the P sources for any P rate. The only exceptions were for the first and third years of one site (O'Brien), when TSP showed higher residual soil P than struvite as measured by the three test methods. It is puzzling that this difference was not observed for the second year or lower P rates. The soil properties measured (such as texture, pH, and extractable cations) did not allow for a reasonable explanation, and we believe differences resulted from experimental error or random variability.

Overall, we conclude that, for corn-soybean rotations in the three Iowa soils included in the study, P recovered as struvite from the aqueous stream of corn processing for bioenergy has crop P availability similar to or higher than P fertilizer. In the near future, these results will be relevant for production agriculture and for environmental concerns because large amounts of P can be recovered as struvite from crop fiber processing for bioenergy and used for crops instead of being disposed of as a waste.

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TABLES

Table 1. Trial sites location, soils, and selected physical and chemical properties.

Site information	Trial sites		
County	Boone	Floyd	O'Brien
Soil series	Webster	Floyd	Marcus
Soil classification	fine-loamy, mixed, superactive, mesic, Typic Endoaquolls	fine-loamy, mixed, superactive, mesic, Aquic Pachic Hapludolls	fine-silty, mixed, superactive, mesic, Typic Endoaquolls
Textural class	silt loam	loam	silty clay
Clay (g kg^{-1})	220	200	420
Silt (g kg^{-1})	570	390	510
Sand (g kg^{-1})	210	410	70
pH	6	6	7
Organic matter (g kg^{-1})	46	33	50
Bray-1 P (mg kg^{-1})	8	11	12
Olsen P (mg kg^{-1})	5	5	9
Mehlich-3 P (mg kg^{-1})	8	9	13
Mehlich-3 K (mg kg^{-1})	148	219	238
Mehlich-3 Ca (mg kg^{-1})	3597	1696	3770
Mehlich-3 Mg (mg kg^{-1})	589	244	827
Mehlich-3 Na (mg kg^{-1})	35	19	30
P test category‡	Very low	Low	Low
K test category‡	Optimum	Very high	Very high

† Average values for surface soil samples (0-15 cm)

‡ Iowa State University interpretation categories for corn and soybean (Sawyer et al., 2002)

Table 2. Site-year specific information.

Crop	Site	Year	Planting Date	Hybrid/Variety	----------------------Precipitation (mm)†-----------------------							
					April	May	June	July	Aug	Total	Avg ‡	Diff §
Corn	Floyd	2009	22-Apr	DeKalb C52-59 RR/VT3	46	44	105	130	62	388	538	-150
	O'Brien	2009	4-May	AgriGold 6325VT3	100	223	77	99	53	552	461	91
	Boone	2010	4-May	Pioneer 35F44	93	92	284	173	285	927	593	334
Soybean	Floyd	2010	4-May	Asgrow 2330 RR2	64	45	232	214	107	662	538	124
	O'Brien	2010	17-May	Kruger K201	86	96	235	127	51	594	461	133
	Boone	2011	19-May	Pioneer 92Y60	111	117	128	99	76	532	593	-61
Corn	Floyd	2011	6-May	Pioneer 0448XR RR/HXX	76	129	135	80	54	474	538	-64
	O'Brien	2011	6-May	Pioneer PO115Xr	108	100	108	99	110	524	461	63
	Boone	2012	18-May	Pioneer 448RR	128	72	80	62	76	418	593	-175

† Data from closer climate station (http://mesonet.agron.iastate.edu/climodat)

‡ Rainfall average of April to August period across 30 years (1979 to 2008)

§ Deviation of the total period rainfall from the 30 year average for the period (1979-2008)

Table 3. Early plant dry weight (DW), P concentration, and P uptake of corn at the V5 to V6 stage as affected by the P sources and rates.

Site	P Source	P application rate (kg P ha^{-1})								Statistics			
		0	12	24	36	48	72	120	Mean †	Source	Int ‡	Model	YMR §
		Plant DW (g/plant^{-1})								--- $P > F$ ---			kg P ha^{-1}
Boone	Struvite	8.18	8.64	9.39	9.62	10.10	11.01	12.43	10.20	0.98	0.03	Linear	120
	Fertilizer		9.84	9.24	10.56	9.94	11.20	10.43	10.20			Quad.	83
Floyd	Struvite	3.86	4.52	5.41	5.91	6.23	6.98	7.72	6.13	0.01	0.01	Quad.	120
	Fertilizer		4.47	4.72	5.11	5.32	6.40	6.48	5.42			Quad.	120
O'Brien	Struvite	4.28	4.46	4.55	4.91	5.19	5.12	6.32	5.09	0.19	0.59	Linear	120
	Fertilizer		4.82	4.46	4.43	4.94	4.92	5.78	4.89				
		Plant P concentration (g/kg^{-1})											
Boone	Struvite	2.68	2.63	3.18	3.39	3.63	4.00	4.63	3.57	0.41	0.32	Quad.	120
	Fertilizer		2.95	3.05	3.70	4.03	4.17	4.16	3.68				
Floyd	Struvite	2.61	2.97	3.23	3.55	3.77	3.80	3.97	3.55	0.96	0.06	Quad.	120
	Fertilizer		3.15	3.25	3.43	3.40	3.83	4.20	3.54				
O'Brien	Struvite	3.18	3.00	3.17	3.37	3.60	3.75	3.70	3.43	0.41	0.84	Quad.	120
	Fertilizer		3.20	3.43	3.37	3.57	3.73	3.70	3.50				
		Plant P uptake (mg/plant^{-1})											
Boone	Struvite	21.9	22.7	29.8	32.5	36.4	44.2	57.8	37.2	0.75	0.01	Linear	120
	Fertilizer		29.0	28.9	39.2	40.0	46.5	43.2	37.8			Quad.	91
Floyd	Struvite	10.0	13.4	17.6	20.9	23.4	26.5	30.7	22.1	0.01	0.04	Quad.	120
	Fertilizer		14.0	15.3	17.5	18.1	24.6	27.2	19.5			Quad.	120
O'Brien	Struvite	13.6	13.4	14.4	16.5	18.7	19.2	23.4	17.6	0.60	0.59	Linear	120
	Fertilizer		15.4	15.5	14.9	17.6	18.4	21.4	17.2				

† Source means excluding the control.

‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).

§ YMR, yield-maximizing rate according to models fit to each source with an interaction significant at $P < 0.05$ or to means with no interaction. The highest applied rate is indicated for models without an estimated maximum within the applied rates range.

Table 4. First year corn grain yield, P concentration, and P accumulation.

		P application rate (kg P ha^{-1})								Statistics			
Site	P Source	0	12	24	36	48	72	120	Mean †	Source	Int ‡	Model and MR §	
		---------------------------- Grain Yield (Mg ha^{-1}) -------------------------								--- $P > F$ ---			kg P ha^{-1}
Boone	Struvite	7.95	8.88	9.63	10.20	10.27	10.63	10.53	10.02	< 0.01	< 0.01	QP	60.9
	Fertilizer		8.77	9.67	9.94	9.98	10.05	7.68	9.35			Qua	57.8
Floyd	Struvite	11.68	12.92	13.40	13.57	13.71	14.02	13.92	13.59	0.99	0.96	QP	46.9
	Fertilizer		12.77	13.29	13.72	13.70	14.07	13.99	13.59				
O'Brien	Struvite	10.35	10.65	11.13	11.78	12.11	12.35	12.52	11.76	0.66	0.94	QP	97.1
	Fertilizer		10.79	11.05	11.42	12.00	12.45	12.43	11.69				
		----------------------- Grain P concentration (g kg^{-1}) --------------------											
Boone	Struvite	2.43	2.65	2.80	2.85	2.80	2.98	3.05	2.85	0.41	0.96	Exp	120
	Fertilizer		2.78	2.90	2.88	2.90	2.95	3.03	2.90				
Floyd	Struvite	1.69	1.83	1.90	2.00	2.00	2.17	2.33	2.04	0.08	0.97	Lin	120
	Fertilizer		1.77	1.80	1.90	1.93	2.10	2.33	1.97				
O'Brien	Struvite	1.52	1.53	1.57	1.63	1.63	1.70	1.77	1.64	0.72	0.94	Quad	120
	Fertilizer		1.52	1.57	1.58	1.70	1.77	1.78	1.65				
		---------------------- Grain P accumulation (kg ha^{-1}) --------------------											
Boone	Struvite	19.18	23.54	26.96	29.06	28.75	31.61	32.12	28.67	0.04	< 0.01	Exp	120
	Fertilizer		24.34	28.04	28.58	28.95	29.65	23.22	27.13			Quad	64.4
Floyd	Struvite	19.73	23.69	25.45	27.15	27.43	30.38	32.48	27.76	0.10	0.96	Quad	120
	Fertilizer		22.56	23.93	26.06	26.49	29.55	32.64	26.87				
O'Brien	Struvite	15.70	16.33	17.44	19.24	19.79	20.99	22.13	19.32	0.86	0.84	Quad	120
	Fertilizer		16.36	17.32	18.09	20.40	21.99	22.17	19.39				

† Source means excluding the control.
‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).
§ QP, quadratic-plateau; MR, estimated rate for the maximum by models fit to each source with a significant interaction ($P < 0.05$) or to means with no interaction. The highest rate is shown for models without a maximum within the applied rates range.

Table 5. Second year soybean grain yield, P concentration, and P accumulation.

		P application rate (kg P ha^{-1})								Statistics			
Site	P Source	0	12	24	36	48	72	120	Mean †	Source	Int ‡	Model and MR §	
		Yield (Mg ha^{-1})								--- P > F ---			kg P ha^{-1}
Boone	Struvite	3.90	4.06	4.15	4.22	4.30	4.32	4.42	4.24	0.44	0.83	Quad	120
	Fertilizer		4.02	4.13	4.17	4.37	4.48	4.56	4.29				
Floyd	Struvite	4.30	4.46	4.68	4.74	4.82	4.85	4.83	4.73	0.78	0.86	QP	63.5
	Fertilizer		4.55	4.62	4.66	4.82	4.82	4.85	4.72				
O'Brien	Struvite	2.83	3.01	2.99	3.15	3.08	3.25	3.19	3.11	0.27	0.92	Exp	120
	Fertilizer		3.15	3.02	3.25	3.28	3.27	3.15	3.19				
		Grain P concentration (g kg^{-1})											
Boone	Struvite	3.73	3.90	4.13	4.05	4.50	4.78	4.83	4.36	0.56	0.99	Quad	120
	Fertilizer		3.80	4.05	4.00	4.33	4.73	4.90	4.30				
Floyd	Struvite	4.23	4.37	4.53	5.03	5.20	5.47	5.53	5.02	0.24	0.55	Quad	120
	Fertilizer		4.37	4.67	4.77	4.97	5.27	5.57	4.93				
O'Brien	Struvite	4.92	5.02	5.03	5.23	5.20	5.23	5.40	5.19	0.51	0.82	Lin	120
	Fertilizer		5.17	5.00	5.10	5.33	5.23	5.60	5.24				
		Grain P accumulation (kg ha^{-1})											
Boone	Struvite	14.52	15.84	17.10	17.09	19.34	20.63	21.32	18.55	0.93	0.96	Quad	120
	Fertilizer		15.26	16.74	16.70	18.91	21.19	22.34	18.52				
Floyd	Struvite	18.20	19.46	21.22	23.85	25.05	26.53	26.74	23.81	0.24	0.55	Quad	120
	Fertilizer		19.85	21.58	22.22	23.94	25.37	26.97	23.32				
O'Brien	Struvite	13.91	15.11	15.06	16.47	16.04	17.02	17.21	16.15	0.19	0.85	Exp	120
	Fertilizer		16.26	15.11	16.56	17.50	17.10	17.63	16.69				

† Source means excluding the control.
‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).
§ QP, quadratic-plateau; MR, estimated rate for the maximum by models fit to source means since there was no significant interaction (P < 0.05) with P rate. The highest rate is shown for models without a maximum within the applied rates range.

Table 6. Third year corn grain yield, P concentration, and P accumulation.

		P application rate (kg P ha^{-1}) †							Statistics			
Site	P Source	0	24	36	48	72	120	Mean ‡	Source	Int §	Model and MR ¶	
		Yield (Mg ha^{-1})							--- $P > F$ ---			kg P ha^{-1}
Boone	Struvite	8.76	9.98	10.34	11.18	11.60	11.71	10.96	0.71	0.91	QP	88.3
	Fertilizer		9.83	10.60	11.22	11.36	11.40	10.88				
Floyd	Struvite	11.85	12.66	13.06	13.26	14.11	14.75	13.57	0.80	0.99	Quad	120
	Fertilizer		12.60	13.10	13.29	13.98	14.55	13.50				
O'Brien	Struvite	11.45	11.72	11.82	11.77	11.89	12.26	11.89	0.80	0.87	Lin	120
	Fertilizer		11.61	11.66	11.86	12.08	12.43	11.93				
		Grain P concentration (g kg^{-1})										
Boone	Struvite	1.58	1.63	1.64	1.68	1.83	1.90	1.73	0.56	0.96	Lin	120
	Fertilizer		1.65	1.64	1.65	1.75	1.83	1.70				
Floyd	Struvite	1.67	1.73	1.70	1.67	1.87	2.23	1.84	0.91	0.81	Quad	120
	Fertilizer		1.67	1.70	1.77	1.77	2.27	1.83				
O'Brien	Struvite	2.12	2.10	2.19	2.23	2.27	2.37	2.23	0.74	0.99	Lin	120
	Fertilizer		2.13	2.20	2.24	2.30	2.40	2.26				
		Grain P accumulation (kg ha^{-1})										
Boone	Struvite	13.80	16.22	16.93	18.73	21.17	22.24	19.06	0.43	0.88	Quad	120
	Fertilizer		16.23	17.36	18.51	19.89	20.81	18.56				
Floyd	Struvite	19.75	21.94	22.21	22.11	26.34	32.95	25.11	0.75	0.82	Quad	120
	Fertilizer		21.01	22.26	23.48	24.69	32.99	24.89				
O'Brien	Struvite	24.24	24.60	25.88	26.30	26.95	29.02	26.55	0.72	0.99	Lin	120
	Fertilizer		24.77	25.65	26.62	27.78	29.83	26.93				

† Data for the 12-kg P rate are not shown because additional P was applied.
‡ Source means excluding the control.
§ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).
¶ QP, quadratic-plateau; MR, estimated rate for the maximum by models fit to source means since there was no significant interaction ($P < 0.05$) with P rate. The highest rate is shown for models without a maximum within the applied rates range.

Table 7. First- year post-harvest soil-test P (Bray-1, Mehlich-3 and Olsen) for three trial sites.

		P application rate (kg P ha^{-1})								Statistics		
Site	P Source	0	12	24	36	48	72	120	Mean †	Source	Int ‡	Model §
		Bray-1 P (mg kg^{-1})								----- $P > F$ ----		
Boone	Struvite	8.0	10.8	12.4	14.8	16.3	20.9	30.4	18.0	0.32	0.38	Lin
	Fertilizer		9.4	11.5	14.3	16.6	26.8	33.5	18.7			
Floyd	Struvite	8.4	9.2	9.0	16.0	20.2	27.5	40.2	20.3	0.37	0.74	Lin
	Fertilizer		10.2	11.3	13.5	17.8	24.5	38.0	19.2			
O'Brien	Struvite	10.0	10.2	13.5	19.3	18.2	20.2	31.0	18.9	0.05	0.01	Quad
	Fertilizer		14.7	10.8	12.2	22.2	24.3	46.0	21.3			Lin
		Olsen P (mg kg^{-1})										
Boone	Struvite	4.6	5.5	5.8	6.9	7.6	11.0	15.5	8.7	0.29	0.74	Lin
	Fertilizer		4.6	6.0	7.1	8.1	12.6	17.6	9.4			
Floyd	Struvite	5.8	5.7	5.2	8.8	12.1	14.5	20.2	11.1	0.72	0.47	Lin
	Fertilizer		5.5	7.3	11.2	8.3	13.5	18.5	10.7			
O'Brien	Struvite	5.6	6.2	7.9	10.3	10.5	11.3	16.1	10.4	0.01	0.03	Quad
	Fertilizer		10.2	8.0	9.0	13.0	11.8	24.0	12.7			Lin
		Mehlich-3 P (mg kg^{-1})										
Boone	Struvite	8.0	10.4	12.0	14.5	15.4	21.1	29.8	17.2	0.34	0.49	Lin
	Fertilizer		8.8	11.3	13.9	16.6	24.5	34.4	18.2			
Floyd	Struvite	7.3	7.5	9.8	16.0	18.5	26.8	38.7	19.5	0.12	0.46	Lin
	Fertilizer		8.5	10.2	11.5	15.7	21.9	39.0	17.8			
O'Brien	Struvite	10.9	12.3	15.2	20.8	21.0	23.7	33.2	21.0	0.30	0.03	Quad
	Fertilizer		15.0	12.7	13.7	23.0	24.3	48.8	22.9			Lin

† Source means excluding the control.
‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).
§ All quadratic models increased with increasing increments to a maximum at rates higher than the highest applied (120 kg P ha^{-1}).

Table 8. Second- year post-harvest soil-test P (Bray-1, Mehlich-3 and Olsen) for three trial sites.

		P application rate (kg P ha^{-1})								Statistics		
Site	P Source	0	12	24	36	48	72	120	Mean †	Source	Int ‡	Model §
		------------------------- Bray-1 P (mg kg^{-1}) ----------------------------								------ P > F ------		
Boone	Struvite	7.3	8.3	9.0	10.0	12.0	15.0	22.4	12.8	0.30	0.69	Quad
	Fertilizer		8.0	10.0	9.3	12.0	17.9	23.9	13.5			
Floyd	Struvite	8.3	8.8	10.2	12.7	14.2	20.3	28.8	15.8	0.24	0.98	Quad
	Fertilizer		9.0	9.8	11.0	12.8	18.0	27.2	14.6			
O'Brien	Struvite	8.8	8.5	11.2	14.3	12.2	16.2	21.8	14.0	0.62	0.30	Quad
	Fertilizer		10.7	9.7	9.7	18.5	15.5	24.3	14.7			
		------------------------ Olsen P (mg kg^{-1}) -----------------------------										
Boone	Struvite	3.4	4.1	4.0	4.9	6.4	8.5	12.3	6.7	0.93	0.65	Quad
	Fertilizer		3.5	5.0	3.9	5.5	8.9	13.6	6.7			
Floyd	Struvite	3.9	4.2	4.3	5.8	6.5	10.0	13.0	7.3	0.36	0.14	Quad
	Fertilizer		4.2	5.5	6.7	5.2	7.2	12.7	6.9			
O'Brien	Struvite	5.8	6.2	7.2	8.2	8.8	11.0	14.8	9.4	0.31	0.84	Quad
	Fertilizer		6.0	5.3	5.2	9.7	9.2	15.0	8.4			
		----------------------- Mehlich-3 P (mg kg^{-1}) -------------------------										
Boone	Struvite	6.8	7.9	8.5	9.6	11.6	14.9	20.9	12.2	0.75	0.84	Quad
	Fertilizer		7.5	9.4	8.9	10.8	16.9	21.4	12.5			
Floyd	Struvite	9.0	9.0	10.7	12.5	14.5	21.8	29.8	16.4	0.17	0.94	Quad
	Fertilizer		9.7	9.3	10.8	12.7	18.5	28.4	14.9			
O'Brien	Struvite	9.3	9.3	13.3	14.8	14.2	18.7	26.7	16.2	0.67	0.57	Quad
	Fertilizer		10.8	10.7	11.7	18.5	14.8	26.7	15.5			

† Source means excluding the control.
‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).
§ All models increased with increasing increments to a maximum at rates higher than the highest applied (120 kg P ha^{-1}).

Table 9. Third- year post-harvest soil-test P (Bray-1, Mehlich-3 and Olsen) for three trial sites.

Site	P Source	P application rate (kg P ha^{-1})							Statistics		
		0	24	36	48	72	120	Mean †	Source	Int ‡	Model §
		----------------------- Bray-1 P (mg kg^{-1}) --------------------------							----- $P > F$ -----		
Boone	Struvite	6.3	7.9	8.8	9.4	12.4	17.0	11.1	0.41	0.96	Quad
	Fertilizer		7.8	7.6	8.1	11.4	17.3	10.4			
Floyd	Struvite	7.7	8.5	11.0	9.8	13.8	16.2	11.9	0.88	0.52	Lin
	Fertilizer		8.8	9.2	9.7	13.7	17.5	11.8			
O'Brien	Struvite	7.6	9.0	10.7	9.5	14.3	17.5	12.2	0.17	0.01	Quad
	Fertilizer		8.0	10.0	12.2	10.8	26.8	13.6			Lin
		------------------------ Olsen P (mg kg^{-1}) ---------------------------									
Boone	Struvite	2.2	2.8	3.1	3.6	4.9	6.6	4.2	0.35	0.56	Quad
	Fertilizer		2.9	2.1	2.6	4.4	7.3	3.9			
Floyd	Struvite	4.6	4.5	5.8	5.7	7.5	8.0	6.3	0.91	0.06	Quad
	Fertilizer		5.2	5.0	5.3	6.5	9.7	6.3			
O'Brien	Struvite	4.4	5.0	6.4	5.6	8.5	12.7	7.6	0.44	0.03	Quad
	Fertilizer		4.8	5.7	7.8	6.4	16.0	8.1			Quad
		---------------------- Mehlich-3 P (mg kg^{-1}) -----------------------									
Boone	Struvite	5.7	7.0	8.4	8.4	12.3	16.8	10.6	0.23	0.84	Quad
	Fertilizer		7.1	6.5	7.5	10.9	16.8	9.8			
Floyd	Struvite	7.3	8.0	10.0	9.0	12.8	15.8	11.1	0.80	0.74	Lin
	Fertilizer		8.7	8.5	9.5	13.2	16.5	11.3			
O'Brien	Struvite	7.7	9.2	11.3	9.7	15.0	18.8	12.8	0.32	0.01	Quad
	Fertilizer		8.7	9.7	12.2	11.2	28.2	14.0			Lin

† Source means excluding the control.

‡ Int, probability of the interaction or a comparison of the two sources for the highest P rate (see Methods).

§ All quadratic models increased with increasing increments to a maximum at rates higher than the highest applied (120 kg P ha^{-1}).

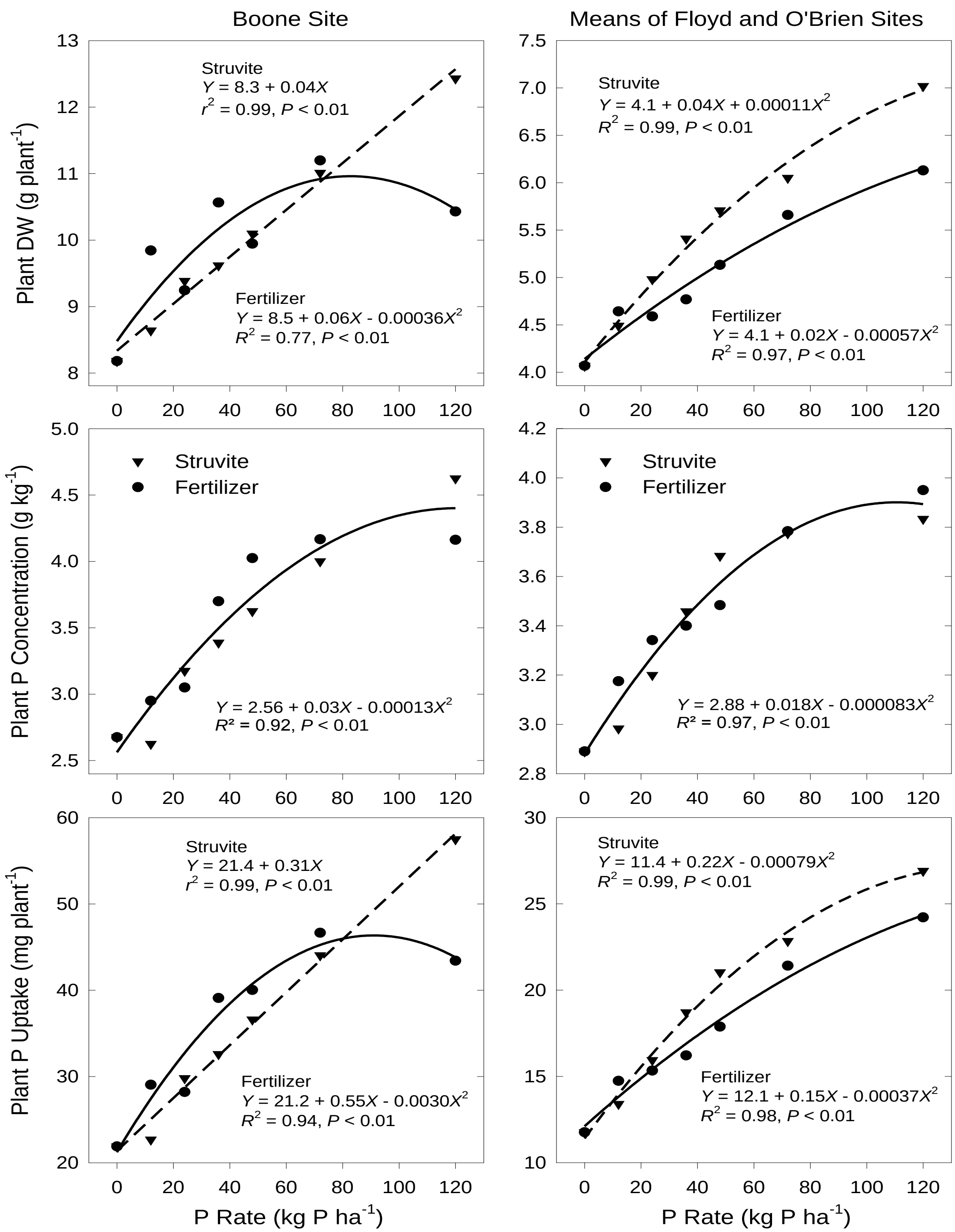

Figure 1. Early plant dry weight (DW), P concentration, and P Uptake of corn at V5to V6 stage as affected by the P sources and rates at Boone and on means of measurements across Floyd and O'Brien sites.

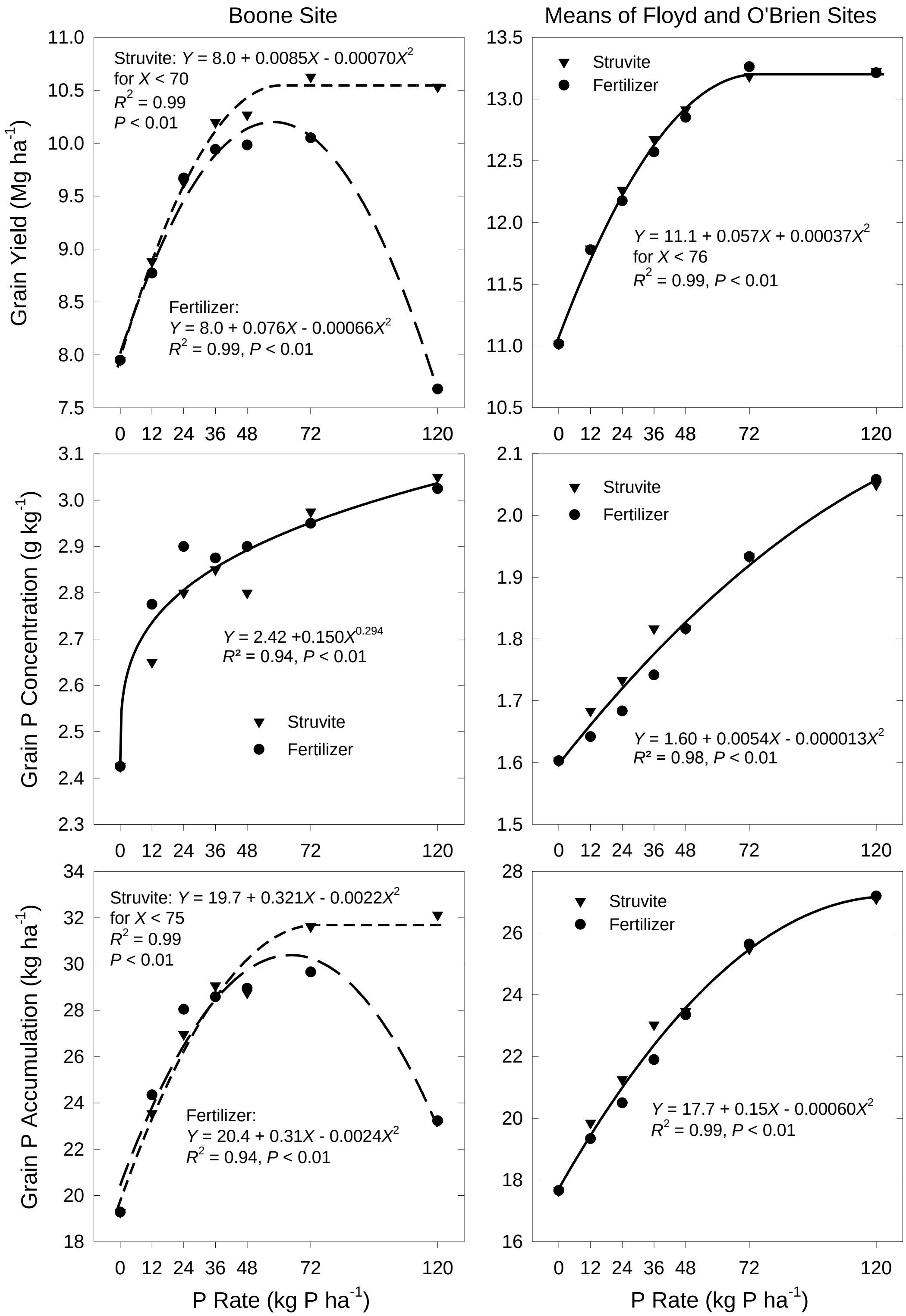

Figure 2. Phosphorus source and rate effects on first-year corn grain measurements at Boone and on means of measurements across Floyd and O'Brien sites.

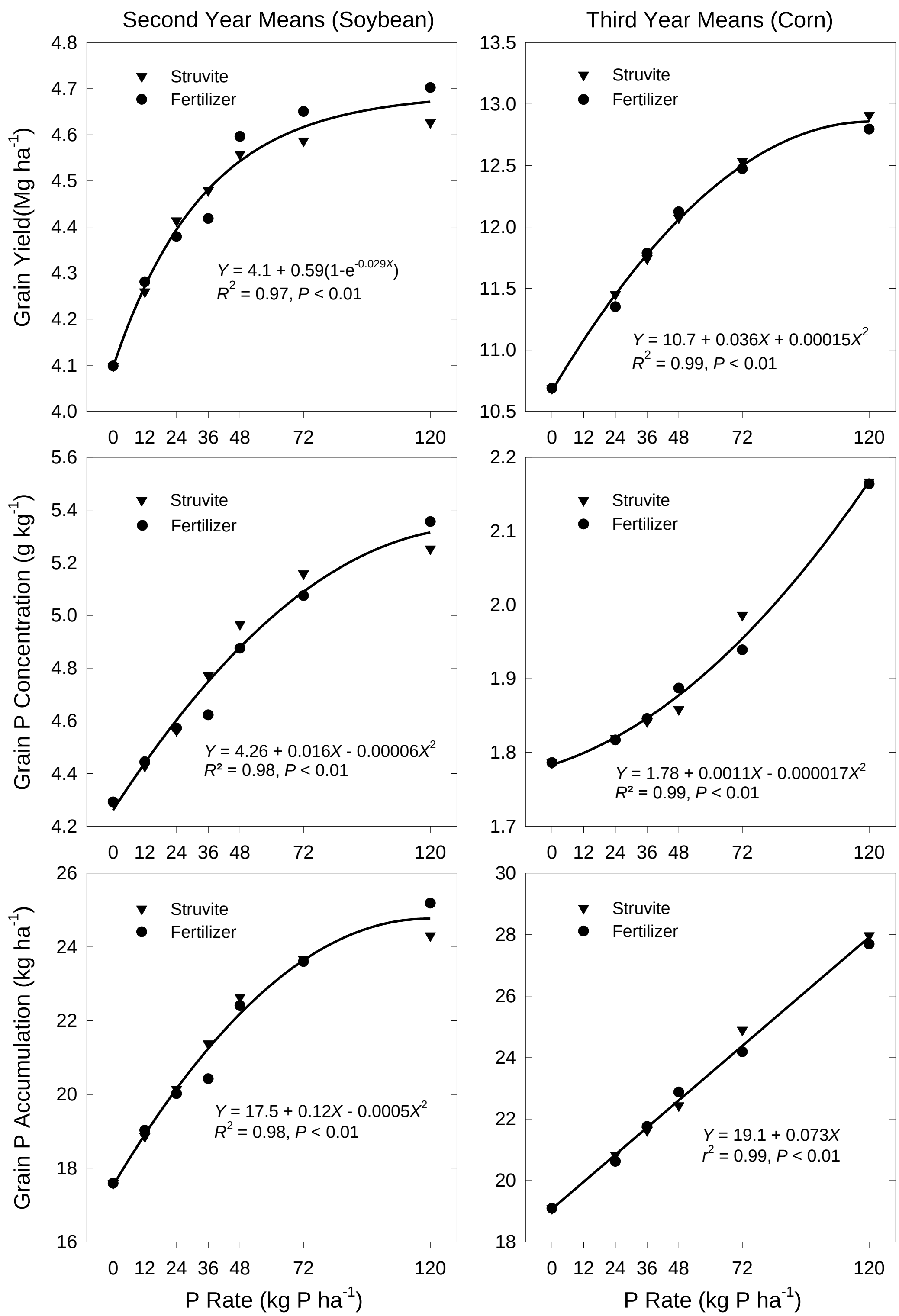

Figure 3. Residual effects P source and rate applied the first year on second- and third-year grain measurements (means across three sites each year).

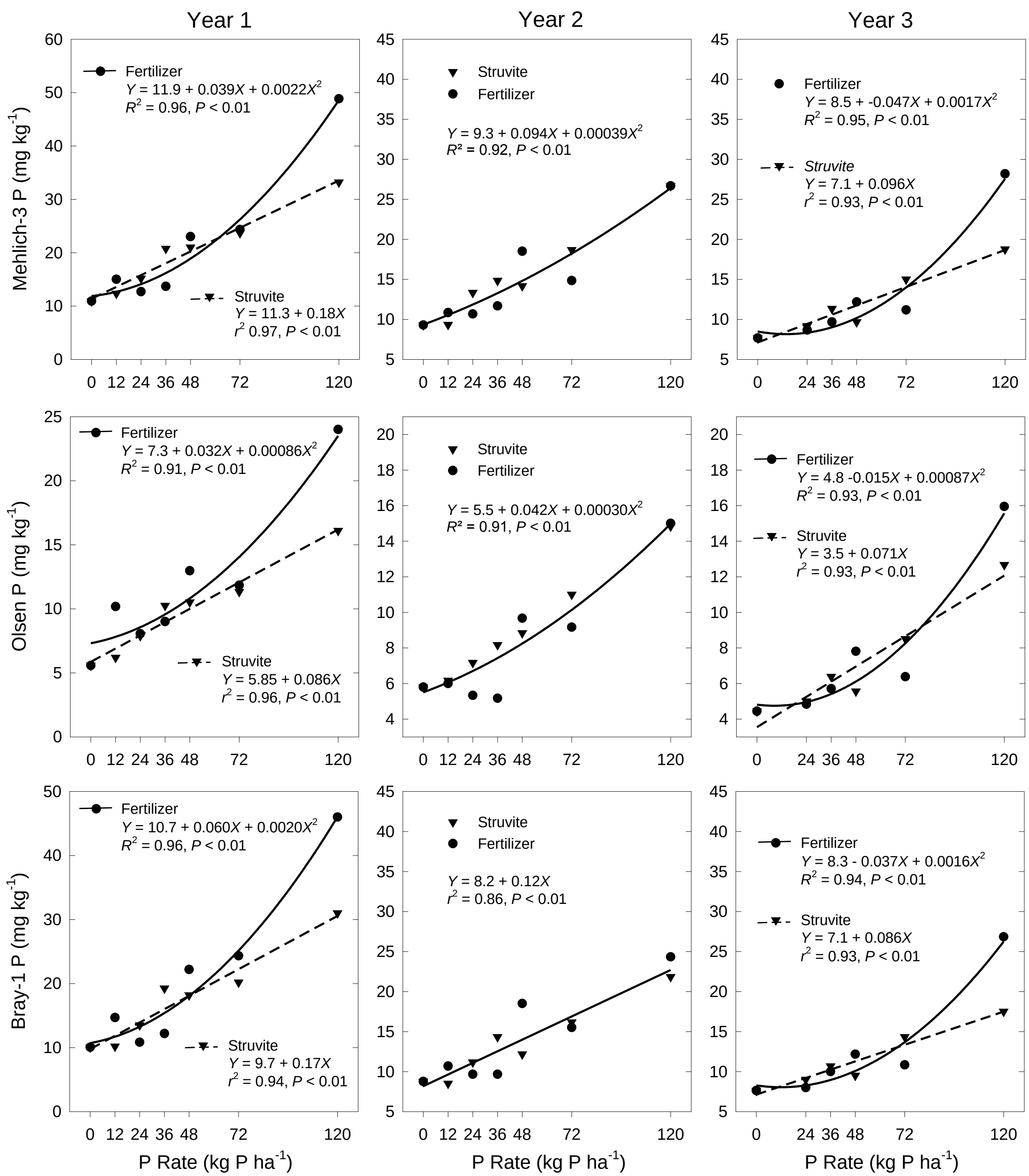

Figure 4. Effects of P sources and rates applied before the first crop at the O'Brien site on soil-test P measured after harvesting the first, second, and third crops of the trials (from data in Tables 7, 8, and 9).

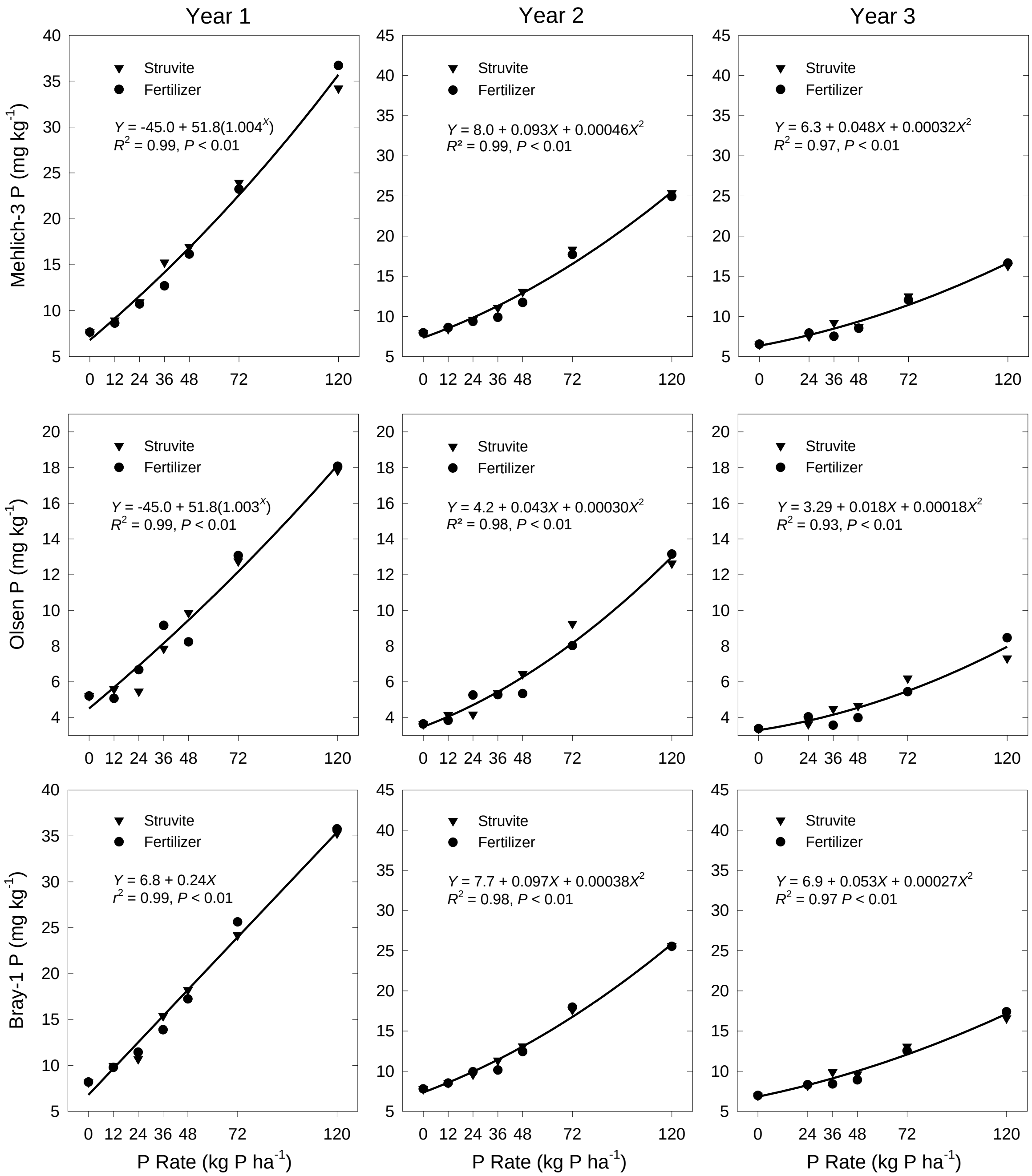

Figure 5. Effects of P sources and rates applied before the first crop at the Boone and Floyd sites on soil-test P measured after harvesting the first, second, and third crops of the trials. Data are means across the two sites from data in Tables 7, 8, and 9).

CHAPTER 3. GENERAL CONCLUSIONS

The objective of this study was to evaluate the phosphorus (P) availability for corn and soybean, of P recovered as struvite from the aqueous stream of corn fiber processing for bioenergy in the field, by comparing it with P fertilizer. To achieve this objective, three-year field plot trials with corn-soybean rotations were established at three sites to evaluate the availability of P in struvite when compared with triple superphosphate (TSP) commercial fertilizer. The trials were established at fields of three Iowa State University research farms: the Northeast Research Farm (Floyd County), the Northwest Research Farm (O'Brien County) near Sutherland, and the Agricultural Engineering/Agronomy Research farms (Boone County) in Central Iowa. The sites chosen had three different typical Iowa soils, which tested Very Low or Low in P according to Iowa State University interpretations (Sawyer et al., 2002). Each trial was evaluated for three years, with corn the first year, soybean the second year, and corn again the third year. Treatments that were replicated three or four times used 0, 12, 24, 36, 48, 72, and 120 kg P ha-1, applied as granulated struvite or granulated TSP. The granule size of struvite used was similar to the fertilizer, and the material had 47 g kg-1 moisture, 117 g kg-1 total P, 6.0 g kg-1 water-soluble P, 99 g kg-1 P soluble in 2% citric acid, and pH 6.9. Measurements were corn aboveground dry matter accumulation (DW), P concentration, and P uptake at the V6 growth stage only in the first year of the study; grain yield, P concentration, and P accumulation; and post-harvest STP each year by the Bray-1, Mehlich-3, and Olsen soil-test P methods.

The soil at the three sites tested below optimum for corn and soybean, so there were very large P rate effects on all plant and soil measurements at the three sites. Results of all corn young plant and grain measurements done in the first year of the study and of all grain measurements in the second and third years showed that the crop availability of struvite P was often similar to TSP and in a few instances it was higher. Struvite was more efficient than TSP at increasing early DW and P uptake at the three sites and for grain yield and P accumulation only at the Boone site in the first year and for the highest P application rate (120 kg P ha-1). These differences occurred because these measurements' values for the highest P rate with TSP were lower than with struvite, and this TSP rate often decreased values when compared with the next lower TSP rate (72 kg P ha-1). We could not find a reasonable explanation with the soil and plant measurements included in the study. The second and third years of the study (corn and soybean, respectively) did not include early plant measurements and evaluated residual effects of the first-year P applications on grain yield, P concentration, and P accumulation. There were no significant P source or interaction source by P rate effects for any grain measurements in the second and third years, and the highest P rate applied prior to the first year maximized values of all measurements in both years in spite of slight differences in response shapes (linear or curvilinear).

Estimates of the crop P availability of P in struvite and TSP by analysis of soil samples collected post-harvest each year by the Bray, M3, and Olsen test methods largely showed no differences between the P sources for any P rate. The only exceptions were for the first and third years of one site (O'Brien), when TSP showed higher residual soil P than struvite as measured by the three test methods. It is puzzling that this difference was not observed for the second year or for lower P rates. The soil properties measured (such as texture, pH, and extractable cations) did not allow for a reasonable explanation of these differences, and we believe they resulted from experimental error or random variability.

Overall, we conclude that, for corn-soybean rotations in the three Iowa soils included in the study, P recovered as struvite from the aqueous stream of corn processing for bioenergy has crop P availability similar to or higher than P fertilizer. In the near future, these results will be relevant for production agriculture and for environmental concerns because large amounts of P can be recovered as struvite from crop fiber processing for bioenergy and used for crops instead of being disposed of as a waste.

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